

Insulator-metal transition in solid hydrogen: Implication of electronic structure calculations for recent experiments.

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Electronic structure calculations for compressed molecular hydrogen are performed to provide more insight into the diversity of phenomena recently observed experimentally. We perform full-potential LAPW calculations and analyze them in terms of a molecular tight-binding model. We show that σ_g and σ_u bands overlap occurs at rather low pressure, while an insulating state persists at specific orientations up to 200 GPa, in accord with previous work, and is due to opening of hybridization gaps at the Fermi level. We also present calculations of electronic properties such as plasma frequencies and electron-vibron coupling.

Experimental data on the behavior of hydrogen at megabar pressures is rapidly emerging as a result of advances in diamond-anvil cell technique. Certain results are clearly established and understood, while a number of questions remain, most of which concern the implication of spectroscopic results for the electronic structure. One issue, in particular, is band overlap metallization. It is well established that at room temperature and below hydrogen under high pressure stays insulating up to at least 150 GPa¹ (which is about tenfold compression, $r_s \approx 1.4$). LDA calculations^{2,3,4,5} give a metallization pressure that strongly depends on the assumed orientation of hydrogen molecules (reported numbers are from 40 to 150 GPa), the strongest metallization tendency being in the structure where all hydrogen molecules are parallel. The reason for such a strong orientational dependence is not completely understood.

A very basic argument for band-overlap metallization of hydrogen is that the insulator-metal transition occurs when the bandwidths of the $1\sigma_g$ and $1\sigma_u$ bands originating from the corresponding molecular orbitals become larger than the splitting of the two molecular levels. One can easily estimate when this should happen using, for instance, Slater's variational LCAO⁶, and assuming the perpendicular orientation (which minimizes the overlap) of neighboring molecules⁷. The answer is $r_s \approx 1.45$. More accurate numerical calculations, starting from Friedli and Ashcroft,², have yielded similar numbers. However, it turns out that even LDA calculations (see, e.g., Refs. 2, 3, 4, 5) render an insulating ground state *in the orientation which minimizes the total energy*. In the local density approximation (LDA), where molecular orbitals are too diffuse, this sort of metallization occurs at even larger r_s .

A detailed microscopic analysis of compressed hydrogen, even in LDA and for clamped nuclei, has not been yet presented. To provide further insight into the available experimental data, we performed full-potential LAPW calculations for hydrogen for different orientations. By mapping the calculated band structure onto the two molecular orbitals nearest-neighbor tight binding model we show how this band structure is formed and why the minimum total energy orientation appears insulating.

Most previous calculations^{3,4,5} used a plane wave expansion for the wave functions. This is a good basis set for the interstitial region; however, close to nuclei it converges slowly. For a standard cut-off of 50 Ry the Fourier expansion of hydrogen $1s$ wave function converges at a nucleus only within 14%. We used the Linearized Augmented Plane Wave method with an MT radius of 0.69 bohr; for $r \geq 0.69$ the error in the aforementioned $1s$ Fourier expansion is about 50 times smaller than for $r = 0$. We found the total energy to be convergent better than 1 mRy, with the cut-off of 44 Ry. We find that the calculations converge relatively slowly with the number of \mathbf{k} -points in the Brillouin zone; we had to use a special \mathbf{k} -point mesh $12 \times 8 \times 8$ corresponding to 96 points in the irreducible edge for the 4-molecule orthorombic structure described below. Most calculations reported here were performed for $r_s = 1.435$ (lattice parameter 3.3 bohr, molecular volume $2.209 \text{ cm}^3/\text{mol}$, $\rho/\rho_0 = 10.5$). The calculated pressure was about 150 GPa at this compression. We also performed some calculations at higher compressions in order to detect the LDA metallization.

The crystal structure of high-pressure phases II and III has not been determined¹. It is generally believed that centers of molecules form an hcp lattice, as they are

known to do to at least 50GPa. At least four distinct optical (Raman and infrared) vibron modes are observed in phase II in hydrogen and deuterium^{1,8}, indicating an orientational ordering of at least four molecules per cell. Phase III has an orientational order different from that of phase II⁹, with one strong Raman and one extremely strong infrared vibron¹. Both vibrons show substantial softening, typically by 200 cm^{-1} between 200 and 100 K, when passing into phase III. The structure considered the most relevant for the high-pressure phases of hydrogen is the Pca₂1 structure which is derived from the hcp-c (in which all molecules are aligned parallel to *c*, space group P6₃/mmc) by doubling the unit cell and making the four molecules in the unit cell to be tilted from *c* by an angle θ and rotated by $\pm\varphi, \pi \pm \varphi$. This structure is known to minimize the electrostatic energy of classical quadrupoles on an hcp lattice, at $\theta \approx 55^\circ$ and $\varphi \approx 43^\circ$. Notably, even at $\rho/\rho_0 \approx 13$ ($r_s \approx 1.35$) the equilibrium orientation, calculated from total energy methods, is similar to this⁴, although quadrupolar interaction is not the dominant anisotropic interaction at this compression. Our computations, described below, give $\theta \approx 62^\circ$ and $\varphi \approx 50^\circ$ at $r_s = 1.435$.

The assumed structure has five degrees of freedom: c/a and b/a , two orientational angles, and the H₂ bond length. We have fixed $b/a = \sqrt{3}$, as in hcp, and optimized the structure with respect to four remaining parameters. We find that c/a is not sensitive to orientation: for the high-symmetry P6₃/mmc structure, i.e. for $\theta = 0$, we find $c/a = 1.59$, while for $(\theta, \varphi) = (62^\circ, 50^\circ)$ orientation it is 1.62. The optimal bond length changes more: for the same c/a (1.59) the bond length *d* in P6₃/mmc structure is 1.42 bohr, while for $(62^\circ, 50^\circ)$ it is 1.48 bohr. Most of our calculations below use $c/a = 1.6$ and $d = 1.5$ bohr.

Fig.1 shows the orientational dependence of the total energy. Note that the potential barrier for librations around $(62^\circ, 90^\circ)$ is rather low, about 280 K. Of course, the calculated energy profile corresponds to coherent rotations. Actual behavior of the system depends on how the energy profile differs when a single molecule is rotating in the field of its neighbors. For a single molecule librating in the potential shown in Fig.1, we can solve the Schrödinger equation for the anharmonic oscillator numerically and find that even at zero temperature the molecule would be freely librating around the average orientation $(62^\circ, 90^\circ)$ with the amplitude of $\approx 40^\circ$ (both for hydrogen and deuterium), thus making a less orientationally ordered phase. If we want to characterize the degree of orientational order, we should introduce an orientational order parameter, which is usually written as a zero-trace tensor $Q_{\alpha\beta} = (3\langle n_\alpha n_\beta \rangle - \delta_{\alpha\beta})/2$, where **n** is the unit vector of the molecule's direction. Principal values of this tensor for axially symmetric librations are $\{Q, -Q/2, -Q/2\}$, and $Q = 1$ for full ordering. Librations described above correspond to $Q_{\alpha a} \approx \{0.5, 0, -0.5\}$, while free rotation around *c*-axis with $\theta = 62^\circ$ gives $Q_{\alpha a} = \{-0.17, 0.085, 0.085\}$.

The first two azimuthal librational eigenstates are about 30 cm^{-1} (7.5 cm^{-1}) and 170 cm^{-1} (100 cm^{-1}) above the saddle point at $(62^\circ, 90^\circ)$ for hydrogen (deuterium). Since $(62^\circ, 90^\circ)$ is a saddle point, azimuthal and polar librations are quite different: Azimuthal librations, as described above, are strongly anharmonic, while polar vibrations, to the contrary, can be treated in the harmonic approximation. Their amplitude reaches $\approx 40^\circ$ at $T \approx 400\text{K}$. The calculated frequency of the polar libron is about 350 cm^{-1} .

One of the most intriguing issue is whether or not the equilibrium geometry is governed by electrostatic forces. The calculated ground state $(62^\circ, 50^\circ)$ is very close to the equilibrium orientation $(55^\circ, 43.5^\circ)$ for the quadrupolar hcp lattice (see, also, Ref. 4). This orientation $(62^\circ, 50^\circ)$ maximizes the insulating gap (actually even small deviations from this orientation render a metallic state). Thus, the band structure energy also favors this orientation. Besides, at the tenfold compression the actual electrostatic interaction differs substantially from the ideal quadrupolar one. These arguments cast doubt about quadrupolar interaction being the main ordering factor. More insight can be gained from comparing calculations with different number of **k**-points. We have performed calculations with a sparser mesh (12 points) and found that the total energy is minimal at $(20^\circ, 90^\circ)$. 12 **k**-points for an 8-atoms unit cell is a sufficiently large number to have the charge density converged. Indeed, we found no substantial difference between the orientational dependence of the electrostatic energy in the both sets of calculations. To the contrary, the one-electron energy orientational dependence is quite different in the two cases (with 12 points, it is not converged yet). Thus, we conclude that the main factor controlling the orientational ordering at about tenfold compression is one-electron (band) energies.

Since the driving force for orientational ordering is the band energy, it is useful to compare the electronic bands for several different orientation. Fig.2a shows the bands (full lines) for the two-molecules-per-cell P6₃/mmc hcp structure. To understand the nature of the relevant bands, we compare the self-consistent band structure with that from two-molecular-orbital tight-binding (TB) model (dashed lines). The TB parameters were $t = 3\text{ eV}$, $E_{\sigma_u} - E_{\sigma_g} = 16.8\text{ eV}$ at $r_s = 1.435$. Only 12 nearest neighbors were taken into account. The lowest states at Γ and X are pure σ_g [actually, $\sigma_g(1) \pm \sigma_g(2)$]. However, the next level at Γ is already the bottom of the σ_u band. Thus the overlap of the σ_g and σ_u bands is very large, of the order of one Rydberg. Note also the third band at Γ , which is the bottom of the $2\sigma_g$ band.

Since the $\sigma_g - \sigma_u$ band overlap occurs at much lower compression ($\rho/\rho_0 \sim 7$), H₂ would be metallic if not for the gaps that open at the Fermi level due to the orientational tilting. Fig.2b shows bands for a less symmetric $(62^\circ, 90^\circ)$ structure (dashed lines), compared to the folded down hcp bands (dotted lines). At several points where two downfolded bands cross in the hcp structure,

the degeneracy is lifted now because of lower symmetry. This band structure is still metallic; the crossings occur at different energies. Nevertheless, the density of states at the Fermi level and correspondingly the one-electron energy is decreased.

If we now move from the (62°, 90°) structure further to the equilibrium orientation (62°, 50°), (full lines in Fig. 2b) we observe that local minima in the conduction band, and maxima of the valence band (which emerged from the band crossings in the P6₃/mmc structure) are now aligned at, respectively, 18 eV and 17 eV, thus forming a considerable gap. Rotating the H₂ molecule influences the positions of these maxima and minima in a complicated way; alignment of the direct gaps such that an indirect gap appears is characteristic for the equilibrium orientation. There is an analogy with the Peierls transition in metals with Fermi surface nesting: if a superstructure exists in which the nesting bands become degenerate, lowering of symmetry removes the degeneracy, decreases the band energy and induces a structural phase transition. An important difference is that there is *no* nesting, and therefore the regular susceptibility would diverge in the high-symmetry phase, as in a Peierls transition. Instead, there is an instability with respect to final rotation of the molecules. Correspondingly, the known problem of the one-dimensional Peierls transition, namely that the divergence in the non-interacting susceptibility may cancel out in the full susceptibility¹¹, does not apply.

Another way to rationalize this result is to use Andersen's force theorem¹², which states that the first-order total energy differences in LDA can be calculated as a sum of the electrostatic energy differences and band energy differences, provided that charge density is not recalculated to self consistency in the perturbed configuration (for instance, if one would ascribe a sphere around each molecule and rotate it rigidly without changing the charge distribution inside the sphere). While it was not done in our calculations (and is technically not possible in LAPW method), the changes of molecular charge density upon rotation are small.

We have also performed calculations for higher compression, but without orientational optimization. The indirect gap closes after further compression by 6.5% ($P \approx 185$ GPa). It is well known¹³ that the LDA considerably underestimates semiconductor gaps. Therefore, not only should hydrogen stay insulating in the pressure range of 150 GPa, but the energy of the gap is likely to be rather large. Of course, dynamical disorder smears the gap, thus one can expect gradual increase of the low-energy absorption with temperature and pressure in a non-Drude manner, with eventual full metallization at pressures larger than at least 185 GPa. Optical experiments do not reveal metallic, Drude-like absorption up to ~ 250 GPa^{14,15}; In the phase III which exists above 150 GPa, strong activity of the infrared vibron with frequency $\nu \approx 4 \times 10^3$ cm⁻¹ (in deuterium $\approx 3 \times 10^3$ cm⁻¹) is well documented¹. This puts an upper limit to the

plasma frequency: if hydrogen is a semi-metal at this pressure, then $\omega_{pl} \lesssim 0.4$ eV.

The main vibron frequency softens discontinuously at the transition to the phase III, which in some papers was attributed to the onset of metallic screening⁵, and keeps softening with cooling (up to $\simeq 200$ cm⁻¹)⁹. Current calculations provide several strong arguments against this point of view. First, as also noticed in previous calculations^{3,4,5}, an arbitrary orientation results in a smaller gap or in the closure of the gap, compared to the optimal orientation. Thus one can expect that at elevated temperature when the molecules do not assume any specific orientation, metallization occurs at lower pressure, and upon heating, not cooling. This would result in hardening of the vibrons with cooling, and not softening, and would also demand that phase boundary line would shift to lower temperature with pressure, opposite to the observed trend^{1,9}.

It is also instructive to estimate the possible effect of metallic screening on vibron frequencies. To do that, we can calculate coupling of the main vibron with conducting electrons, $\lambda = -\Delta\omega/\omega = \sum_{n\mathbf{k}} (\partial\epsilon_{n\mathbf{k}}/\partial R)^2 / 2M\omega^2\delta(\epsilon_{n\mathbf{k}} - E_F)$, where $\Delta\omega$ is the change of the vibron frequency ω due to metallic screening, R is the H-H bond length, M is the proton mass and the deformation potentials ($\partial\epsilon_{n\mathbf{k}}/\partial R$) are the derivatives of one-electron energies with respect to the bond length¹⁶. We have done such calculations for the (φ, 0°) and for (65°, 90°) orientations, using 96 nonequivalent first-principle \mathbf{k} -points interpolated onto the denser mesh of 490 nonequivalent points, using a Fourier interpolation¹⁰. By shifting E_F in the valence band we imitate the effect of different degrees of metallization without doing calculations at the different pressures. Simultaneously we can control the degree of metallization by calculating the plasma frequency $\omega_{pl}^2 = (8\pi e^2/\hbar^2 m_e V_{cell}) \sum_{n\mathbf{k}} (\partial\epsilon_{n\mathbf{k}}/\partial \mathbf{k})^2 \delta(\epsilon_{n\mathbf{k}} - E_F)$ and comparing it with the above-mentioned upper bound. The results are shown on Fig.3. One can see that the effect of possible metallization on the phonon frequencies is much too small to explain the softening.

To summarize, we presented detailed full-potential LAPW calculations for clamped-nuclei molecular hydrogen in the Pca₂1 crystal structure for pressures of 150 GPa and above. The structure was optimized with respect to c/a , H-H bond length, and molecular orientations. We found that orientation that minimizes total energy is close to the equilibrium orientation of classical quadrupoles, although the main driving force for orientational ordering is one-electron (band) energy. Molecular hydrogen remains insulating well above the compression at which $\sigma_g - \sigma_u$ bands start to overlap, because at the equilibrium orientation $\sigma_g - \sigma_u$ band crossings occur close to Fermi energy, so that the hybridization open a dielectric gap. On the other hand, dynamical disorder due to zero-point motion will transform the dielectric gap into a pseudogap. We also have calculated electron-vibron cou-

pling constant and found that it cannot account for the 5% vibron softening in Phase III, which must be related primarily with new orientational ordering in this phase.

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FIG. 2. (a) LAPW energy bands for the hcp structure, $P6_3/mmc$, compared with a (dash lines) two-molecular-orbitals tight-binding model, (b) LAPW energy bands for Pca_{21} structure in $(0^\circ, \varphi)$ orientation (downfolded $P6_3/mmc$ structure, dotted lines), $(62^\circ, 90^\circ)$ (dash lines) and $(62^\circ, 50^\circ)$ orientations.

FIG. 3. Plasma frequencies and electron-vibron coupling constant for $(62^\circ, 90^\circ)$ orientation. Experimental upper limit for $\hbar\omega_p$, ≈ 0.4 eV, is also shown.

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FIG. 1. Orientational dependence of the total energy of Pca_{21} hydrogen. Radial coordinate, θ , is the polar angle and angular coordinate, φ , is the azimuthal angle. Lines are guides for eye.

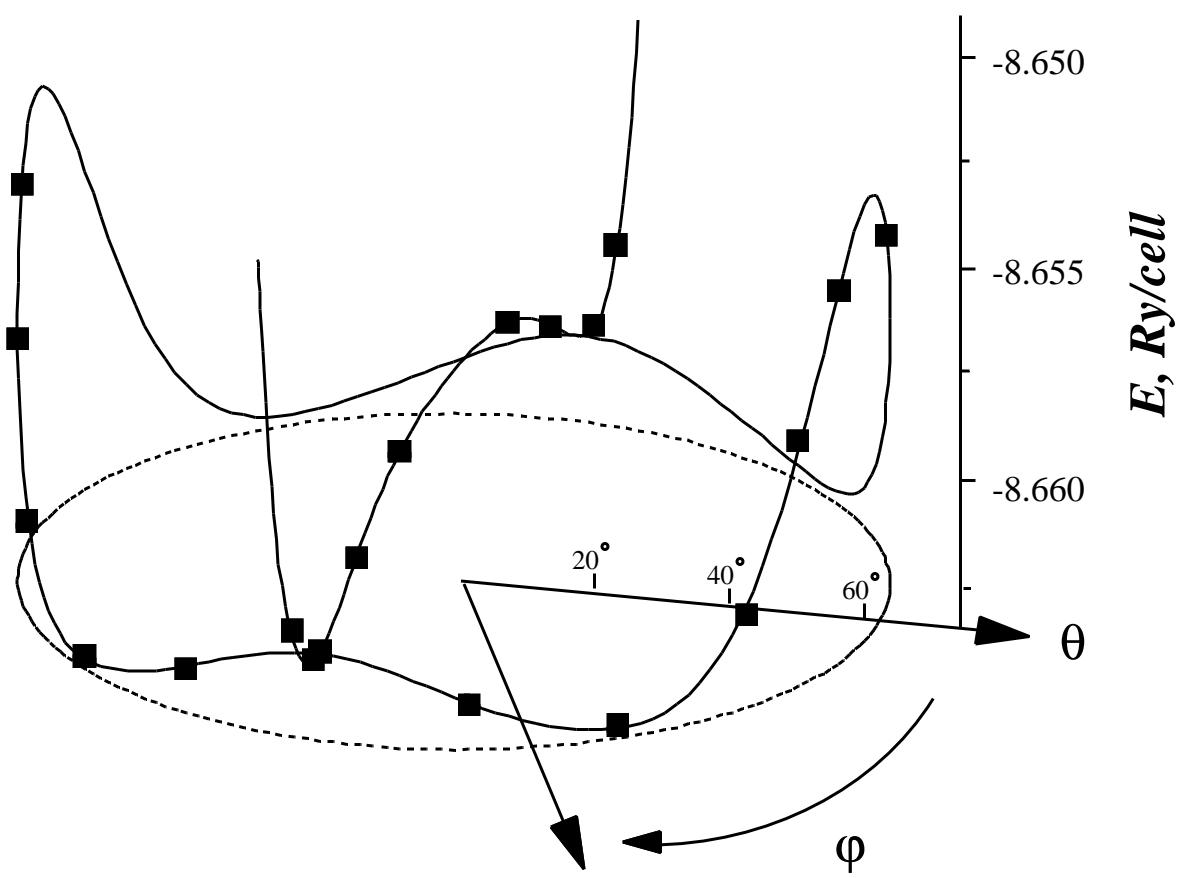


Fig. 1

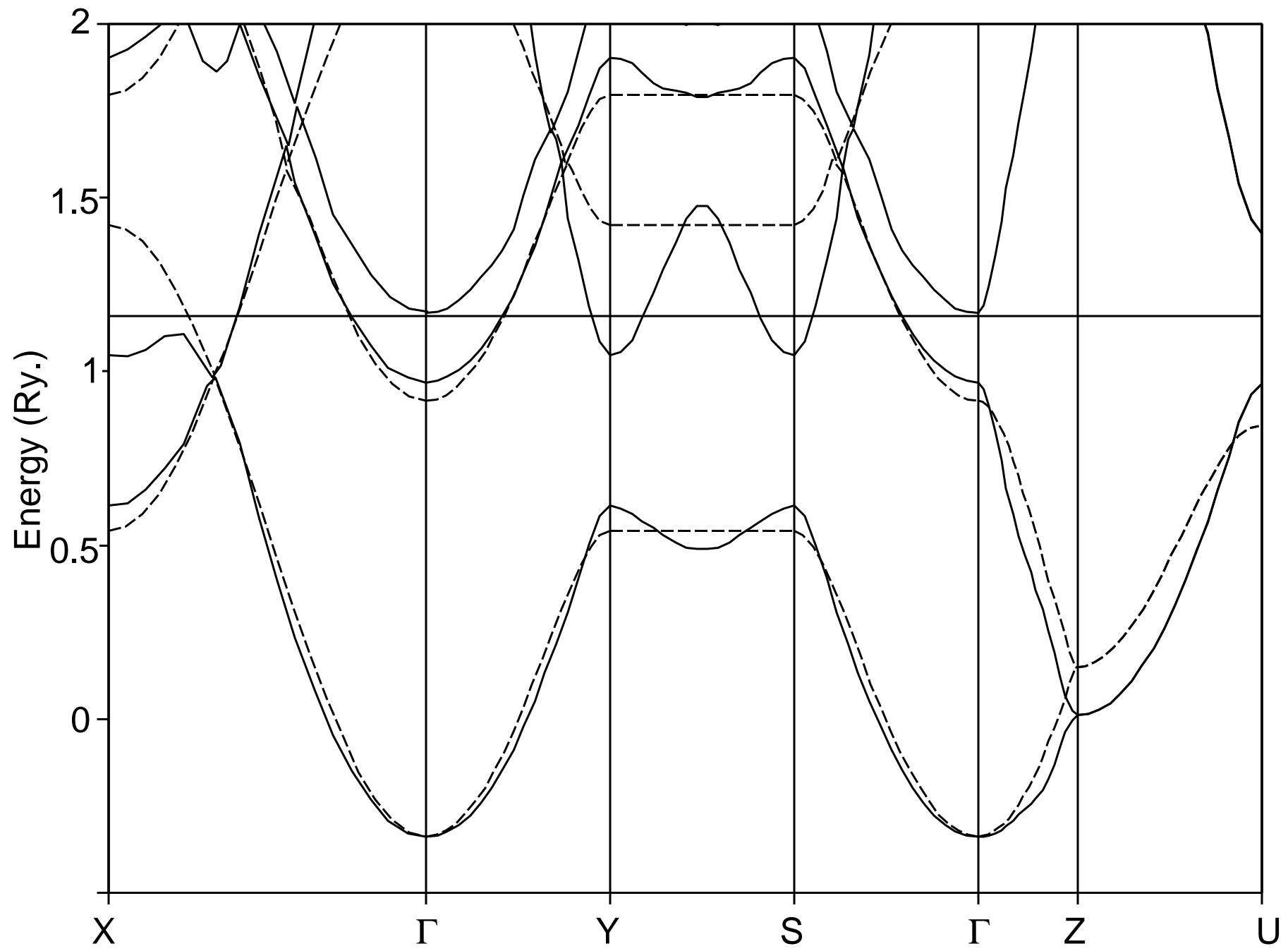


Fig. 2a

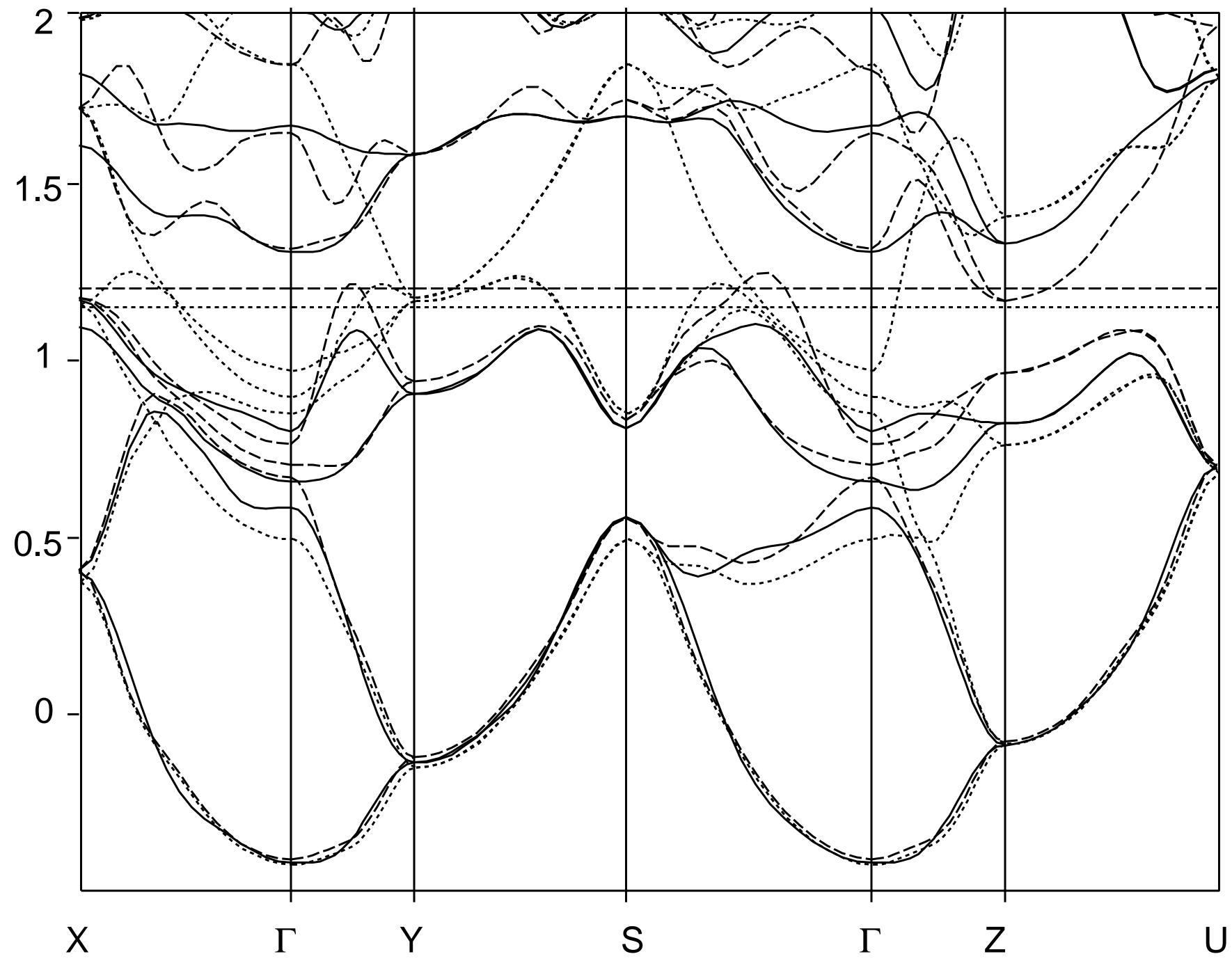


Fig. 2b

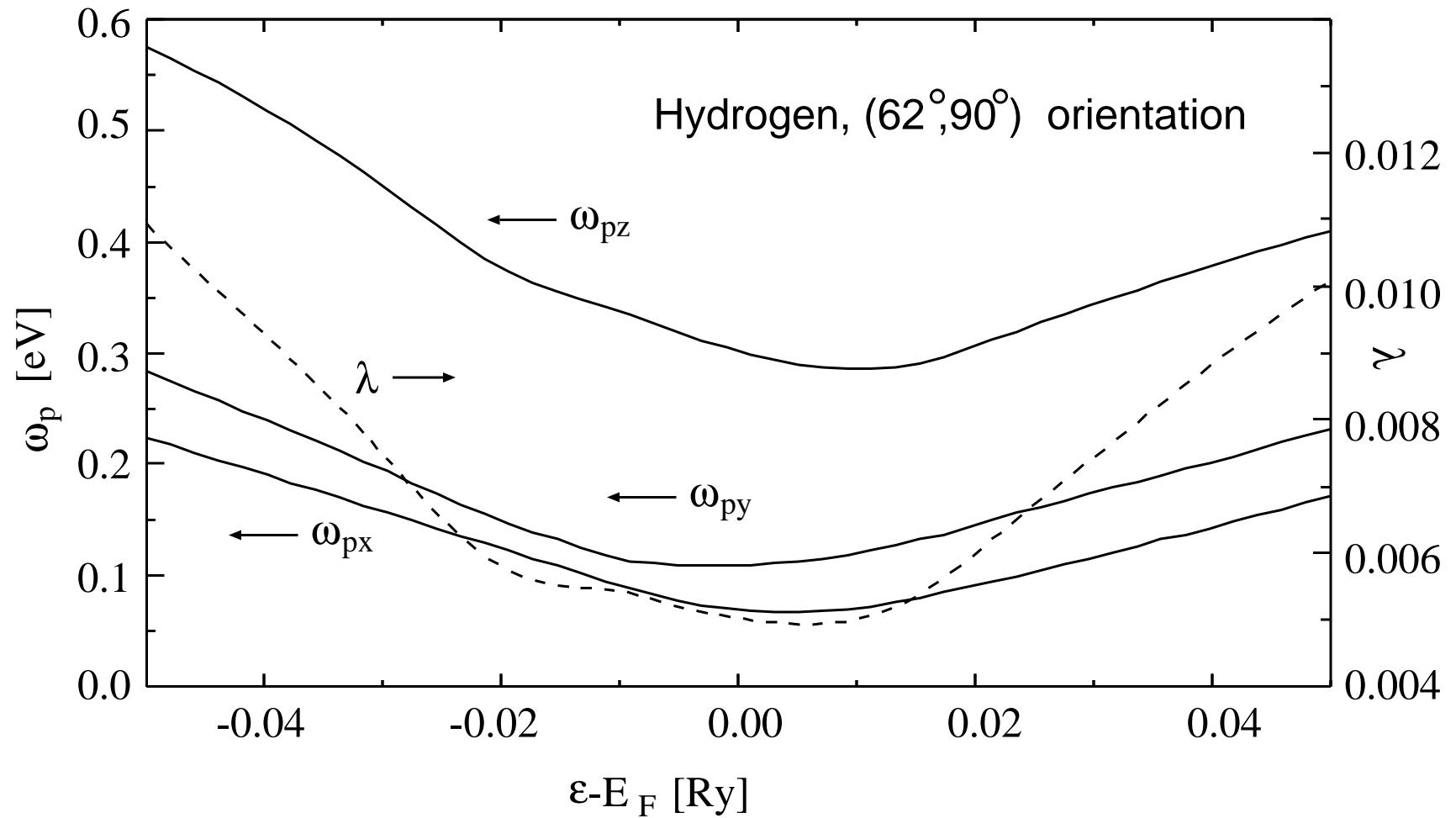


Fig. 3